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MOLYBDENUM HEXAFLUORIDE MoF_6

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MOLYBDENUM HEXAFLUORIDE MoF_6

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ABSTRACT. MoF_6 is generally prepared by direct synthesis of its components. The molecule is entirely symmetrical in structure; the metal atom is located in the center of an octahedron, the apexes of which are occupied by fluorine atoms. When cold, this compound appears as a crystallized white solid body. It melts around 17.5°C and boils around 35°C under air pressure. Very sensitive to hydrolysis and reduction, molybdenum hexafluoride forms addition compounds with sodium, potassium, rubidium, and cesium flourides. It also forms complex compounds with nitrile and nitrosyl fluorides and nitrogen oxides. The reactivity of this symmetrical molecule shows the nonsaturation properties of molybdenum regarding coordination. Inversely, the high inertia of sulfur and seleni-m hexafluoride molecules, which are similar, is to be noted.

1. Introduction.

Molybdenum, of the 6a transition group, is one of the numerous metals or /1* metalloids that yield a volatile hexavalent compound with fluorine. Let us mention among then MoF_6, WF_6, UF_6, PuF_6, NpF_6, TeF_6, ReF_6, SF_6, SeF_6, OsF_6, etc.

Many of these compounds have a similar structure and very close chemical properties. The strucutres of said formula XY_6 molecules, and particularly the structure of MoF_6, have been studied by many investigators. Let us mention here the remarkable synthesis of B. Weinstock [1] on the comparative properties of these different hexafluorides.

Other studies have dealt with the complexes that said moleculcs are capable of forming with certain fluorides, in particular MoF_6, UF_6, and PuF_6, these latter works being generally directed either to the sepatation of fission products obtained by volatilization of irradiated fuels or to the purification of UF_6 by dry means.

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*Numbers in the margin indicated pagination in the foreign text.

We express our appreciation to Mrs. Courtot and Mr. Simon, of the Document Service, for their valuable assistance in the preparation of this paper.

2. Preparations

2.1. By Direct Action of Fluorine on the Metal

The preparation of molybdenum hexafluoride was described for the first time by Ruff and collaborators [2, 3], who prepared it in 1907 by causing dry fluorine at about 60° to react directly with the powdered metal placed in a platinum tube.

Fluorine can be diluted in a nitrogen current [4].

The reaction can also be carried out at a higher temperature (315°C) in a nickel apparatus, where yield is then 78% [5].

Reaction can also take place in a copper tube [6]. The product obtained, collected in a dry and grease-free glass trap, is purified by vacuum distillation [6, 7]. It can be kept indefinitely in the glass vessel at room temperature without formation of SiF_4 [6]. /2

2.2. By Action of Bromine and Chlorine Trifluoride on the Metal or the Corresponding Oxide.

BrF_3 reacts with the metal at 350°C to yield MoF_6 [4], [8].

Nikolaev [9, 10] uses either gaseous chlorine trifluoride, ClF_3, which he causes to react with the metal powder in a quartz reactor or bromine trifluoride, BrF_3, which he causes to react with the oxide MoO_3.

The use of BrF_3 is preferable in the latter case, because the reaction of ClF_3 with the oxide is more violent. The action of BrF_3 can be controlled better.

2.3. MoF_6 is Also Obtained by the Action of Anhydrous Hydrofluoric Acid on Molybdenum Pentachloride in the Presence of Air [7].

2.4. By Action of Sulphur Tetrafluoride on the Corresponding Acid

Excess SF_4 reacts with metallic oxides to yield a fluoride or an oxyfluoride by substitution of two atoms of fluorine for one atom of oxygen. With temperatures ranging between 20 and 500°, depending on the case, MoF_6 was obtained in this manner [11, 12].

2.5. MoF_6 Has Been Prepared by Direct Fluorination in a KF.2HF Electrolyte and Measured by Potentiometry [13] as well as According to the Reaction

$$Mo + 6NOF \cdot 3\,HF \longrightarrow MoF_6 + 6\,NO + 18\,HF \quad (96)$$

3. Methods of Analysis in the Gaseous Phase

3.1. Gas-Liquid Chromatography

This method enables us to measure gaseous MoF_6 in a mixture with another gas. The columns used are polyfluoromonochlorethylene granules impregnated with oil of the same nature. It is thus possible to measure MoF_6 in UF_6 [14] or to measure MoF_6 and W_6 in ClF_3 [15].

3.2. Infrared Spectrophotometry

/3

As the MoF_6 absorption spectrum presents very sensitive infrared absorption bands (reference given in the structure chapter) it is possible in many cases, to measure traces of MoF_6 in a gas with the aid of a spectrophotometer covering the 2.5 - 20 micron range and an analysis cell adapted to fluorinated elements [16, 17].

3.3. Mass Spectrometry

It is possible to measure MoF_6 traces in natural UF_6 using a mass spectrometer with which the peaks corresponding to ions $^{98}MoF_5^+$ and $^{235}UF_5^+$ are compared.

An automatic apparatus based on this principle was developed by the Oak Ridge gaseous diffusion plant [18].

3.4. Atomic Absorption

Gaseous uranium hexafluoride is sent to a premix heater and the molybdenum is determined from a standard curve obtained from synthetic mixtures of uranium hexafluoride and molybdenum hexafluoride. The field of optimal concentration ranges between 10 and 50 ppm of molybdenum by weight in relation to uranium. Ultimate detection is 2 ppm [94].

4. Molecular Structure

Numerous investigators have studied the structure of the regular octahedral molecules of which molybdenum hexafluoride is a part. The metal atom is situated in the center of an octahedron whose summits are occupied by fluorine atoms. This structure is deduced from the study of the infrared

spectra of the Raman spectra, of electron diffraction, as well as from the nuclear magnetic resonance.

4.1. Infrared Spectrum of the Gas

Only the basic V_3 and V_4 bands are active in the infrared. They are observed in the following frequencies expressed in cm^{-1}.

Bands	References [20]		
	(19)		(21)
V_3	742	741	741
V_4	269	260	264
V_6	(240)	(234)	(190)

/4

Band V_6 is inactive in the infrared. The values given in this table were calculated. (See also [22] and [23]).

4.2. Raman Spectra

The basic bands active in the Raman spectrum for the gas and the liquid are:

Bands	(24) liq.	References (20) liq.	[21] gas
V_1	736 cm^{-1}	741 liq.	741 ± 1
V_2	641 cm^{-1}	645 liq.	643 ± 5
V_5	319 cm^{-1}	322 liq.	uncertain

4.3. Absorption Spectrum in the Ultraviolet

The UV absorption spectrum were studied by Tanner and Duncan [24]; they found the following α values for the absorption coefficient:

MoF_6 Pressure Torr	α	cm^{-1}	Å
532	0,09	35 524	(2815)
7,07	6,8	41 494	
2,51	19	43 290	
0,34	57,6	48 356	
0,34	61,4	48 852	
0,34	68,4	49 358	
0,34	82,6	49 702	
0,34	127	50 226	
0,34	176	50 761	(1970)

Tr. Note: Commas indicate decimal points.

The coefficient α is defined according to the following formula:
Tr. Note: Commas indicate decimal points.

$$\text{Ln } I / Io = \alpha \, lo$$

where I/Io is the luminous energy fraction transmitted by a cell, lo in length expressed in cm, filled with gas at a pressure of 760 Torr measured at 0°C.

4.4. Nuclear Magnetic Resonance Spectrum

The high-resolution magnetic resonance spectra of the fluorines of the liquid hexafluorides, MoF_6, WF_6, UF_6, contain essentially a single line in agreement with a regular octahedral structure. For MoF_6 this is a weak and distant field line at 56.4 MHz, with 15,910 ± 40 Hz in relation to the monofluorotrichlorethane taken as reference, Rigny [25]. The relaxation time of the molecule measured at 2.8, 16 and 56.4 MHz is equal to:

$$T_1 = 0{,}85 \pm 0{,}1 \text{ s à } 23°C \quad (25)$$

Blinc and collaborators also studied the NMR spectra and the relaxation time as a function of temperature and of the magnetic field [26].

4.5. Atomic Distances

All of these studies agree in defining a regular octahedral structure of Oh symmetry group--a structure common to numerous molecules of the XY_6 formula. The length of the metal-fluorine link is equal to:

Mo - F = 1,83 Å (27) (28)
Mo - F = 1,840 Å (64)

4.6. Force Constants /6

The force constants calculated and expressed in millidynes/Å are equal to:

K	fdd	f'dd	f	fØ = - fØ''	f'ØØ	f'''ØØ	fdØ = - f'dØ)	Ref.
4,9875	0,2535	0,1561	0,290	0,0810	-0,1045	-0,2112	0,4246	(29)
4,73	0,244							(30)

Tr. Note: Commas indicate decimal points.

fd being the Mo-F force constant.

fdd and f'dd the adjacent and non-adjacent link interaction constants.

fØ the deformation constant.

The other constants being interaction link - link and link - deformation constants.

See also [27] and [31] to [39].

For electron diffraction see [40].

For the Bastiansen-Morino effect see [41].

For the Jahn-Teller effect see [42, 73].

5. Physical Properties

When cold MoF_6 is a snowy crystallized solid; it melts at 17.5° and boils at 35°C at atmospheric pressure [43]. (Figure 1).

5.1. The physical constants are: /7

	Units	Values	References
Molecular Mass		209,93	(46)
Melting Point	°C	17,5	(43) (46) (47)
	°C	17	(23) (44) (45) (48)
	°K	290,76	(57)
Boiling Point at	°C	36,0	(2) (44) (49) (48)
760 mm Hg	°C	35°	(45) (47)

	Units	Values	Reference
Vapor Tension	p in mm Hg t in °C		
for the solid	p in mm Hg T in °K		
For the liquid	p in mm Hg T in °K		
		Valid from 291 to 320°K	
Density of the solid		2.88 at +5°C (calculated)	
Calculated by x diffraction		3.27 at -36°C(calculated) 3.51_9 at 77.16°K(measured)	
Calculated by line displacement		3.51_9 at 77.16°K(calculated) 3.39_3 at 173.83°K(measured)	
		3.39_3 at 173.83°K(calculated)	
Density of the liquid		2.544 at 294.33°K(measured)	
Measure by pycnometer		2.544 at 294.33°K(calculated) 2.491 at 307.08°K(measured) 2.492 at 307.08°K(calculated)	
Magnetic susceptibility		X_S = - (0,124 ± 0,005) 10^{-6} $X_S = -26.10^{-6}$ a 25°C	
Solid transition temperature		263,6 (-9,6°C) 263,48 I 0, 02 -9,8° -8,7	

Note: Commas indicate decimal points.

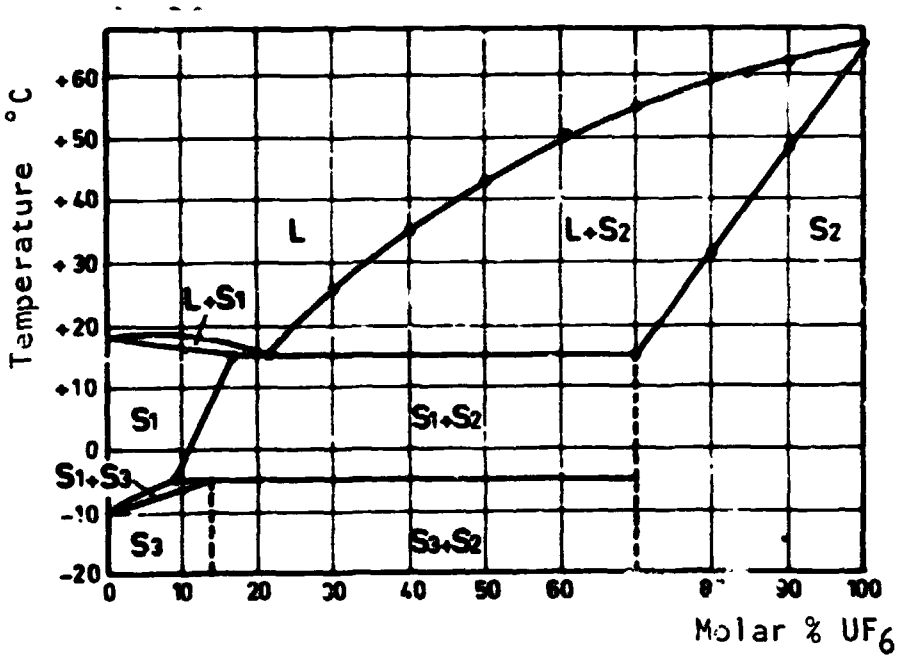

Figure 1. MoF_6 - UF_6 Solid-Liquid Equilibrium Diagram.

5.2. Crystalline Structure

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Molybdenum hexafluoride crystallizes at room temperature following the body centered cubic system; the lattice constant is equal to

at + 10°C a = 6,23 ± 0,01 Å (55)

at + 5°C a = 6,23 ± 0,04 Å (50)

Below the transition point (-9.6°) the orthorhombic structure is obtained. The lattice constants are then

at -20°C a = 9,65 ± 0,02 Å (55)
b = 8,68 ± 0,03 Å
c = 5,05 ± 0,02 Å

at -36°C a = 9,61 ± 0,02 Å
b = 8,75 ± 0,02 Å
c = 5,07 ± 0,02 Å

5.3. Thermodynamic Constants

	Units	Values	Reference
Liquid formation enthalpy at 298.16°K, $\Delta H^\circ f$	Kcal/Mole	- 390,9	(53)
		- 388,6	(54)
		- 392,2	(57)
		- 390,9	(58)
Gas formation enthalpy, $H^\circ f$	Kcal/mole	$- 372,3_5 \pm 0,022$	(59)
	•	- 363,1	(53)
Free liquid formation energy at 298.16°K; $\Delta G^\circ f$	Kcal/mole	- 361,2	(54)
Standard enthropy of gas, S°	cal/Mole deg.	83,77 ± 0,1	(51)
		79,76	(27)
		80,60	(54)
		79,7 ± 0,6	(57)
Standard enthropy of liquid, S°	cal/Mole deg.	62,06 ± 0,06	(57)
		60,1 ; 60,6	(54)
Transition enthalpy of solid; ΔH°_t	cal/Mole	1953,2 ± 2,0	(51)
		1960	(54)
Triple point fusion heat	cal/Mole	1034,2 ± 1,0	(51)
		1060	(54)
Vaporization heat, ΔH°_{298}	cal/Mole	6000	(48)
		6630 ± 25	(51)
Sublimation heat, ΔH°_{298}	cal/Mole	8500	(48)

Tr. Note: Commas indicate decimal points.

The specific heats and thermodynamic functions of gaseous MoF_6 at a pressure of 1 atmosphere calculated at different temperatures yield the following values: /9

T°K	C_p° cal. mole^{-1} deg^{-1}	S° cal. mole^{-1} deg^{-1}	$H^\circ - H_0^\circ$ cal. mole^{-1}	$-(G^\circ - H_0^\circ)/T$ cal. mole^{-1} deg^{-1}
250	26,425	76,454	4 201,6	59,648
273,15	27,544	78,844	4 826,5	61,174
298,15	28,610	81,303	5 528,8	62,760
300	28,683	81,481	5 581,8	62,875
350	30,415	86,038	7 061,1	65,864
400	31,743	90,190	8 616,5	68,649
500	33,565	97,486	11 889	73,707
600	34,700	103,714	15 307	78,202
700	35,441	109,122	18 816	82,241
800	35,948	113,890	22 387	85,905
900	36,307	118,145	26 001	89,255
1 000	36,571	121,985	29 646	92,340

Tr. Note: Commas indicate decimal points.

See also [27] for temperatures comprised between 100 and 1,500°K, [51] for temperatures comprised between 5 and 350°K as well as [60] to [63].

5.4. UF_6 - MoF_6 Liquid-Solid Equilibrium Diagram

The UF_6 - MoF_6 liquid-solid equilibrium diagram was studied by Trevorrow and collaborators [55]. Two solid solutions coexist at low temperatures, one 30% molar MoF_6 in UF_6 and the other 13% molar UF_6 in MoF_6, see Figure 1.

5.5. Solubility in Uranium Hexafluoride and Liquid Hydrofluoric Acid

Mears and collaborators studied the solubility of different fluorides in liquid UF_6 at 70°C [65] for purposes of recovering UF_6 by distillation. The solubility of MoF_6 is more than 22.5% by weight at 38°C. The only point of liquid-vapor equilibrium established by Mears indicates that the behavior of the solution is close to that of an ideal solution.

Trevorrow [68], on the other hand, finds a marked deviation from ideality /10 but the four points established show a great dispersion of results.

Frlec and Hyman studied the solubility of different hexafluorides in liquid hydrofluoric acid [68]. They obtained the following values at room temperature

	Moles / 1 000 g d'HF	Ref.
MoF_6	1,50	(66)
WF_6	3,14	(66)
UF_6	0,49	(67)

Tr. Note: Commas indicate decimal points.

	% in Weight by HF	Ref.
MoF_6	16,5 $\pm$ 1	(98)
WF_6	11,52 $\pm$ 1,5	(98)
UF_6	0,98 $\pm$ 0,5	(98)

Tr. Note: Commas indicate decimal points.

These authors also measured the electric conductivity of these solutions [66]. Nikolaev and collaborators also studied said solubilities [97, 98] at -5°C.

5.6. Recovery of UF_6 Polluted by Molybdenum Hexafluoride by Distillation.

Several papers deal with the distillation of UF_6 - MoF_6 mixtures. In addition to the values of the separation factor measured by Mears [65] and by Trevorrow [68] we find a description of a distilling column [70].

Reference [69] also deals with the distillation of said mixtures.

6. Chemical Properties

As seen in the introduction, molybdenum hexafluoride presents numerous chemical analogies with other hexafluorides, especially with those of tungsten and uranium, which we shall examine.

6.1. Reactions by Addition of MoF_6, WF_6 and UF_6 to Certain Flourides /11

The molybdenum, tungsten and uranium hexafluorides combine with certain alkaline fluorides giving alkaline fluoro-molybdates, tungstates and uranates where the transition metal is in the oxidation six state. Said fluorine salts yield by decomposition or reduction complexes in which the metal has a valence 5 or 4. The following are obtained, in particular with MoF_6:

-from gaseous MoF_6 -- MoF_6 + NaF yield Na MoF_7, Na_2MoF_8 [71, 72, 90, 91].

M_2MoF_6 with (M = K, Rb, Cs) [8] are also obtained.

-in solution in IF_5 [74]

. K_2MoF_8

. Rb MoF_7

. $CsMoF_7$.

Several authors studied the dissociation pressure of the MoF_6 - NaF complexes. They find:

at 100°	0.4 to 4.6 mm Hg	[78]
at 150°	8.4 to 27 mm Hg	[78]
at 200°	64 mm Hg	[78].

Katz obtained the following formulas:

-for the vapor tension of MoF_6 of the equilibrium $MoF_6 + 2\ NaF \rightleftarrows Na_2MoF_8$

$\log P$ mm Hg $= 8.27 \pm 0.07 - (2.87 \times 10^3)/T_K$ [71].

-for the vapor tension of MoF_6 of the equilibrium $Na_2MoF_8 + MoF_6 \rightleftarrows 2\ NaMoF_7$ $\log P$ mm Hg $= 7.29 \pm 0.03 - (1.83 \times 10^3)\ T_K$ [72].

See also [79, 80] and [81] which deal with MoF_6 - NaF complexes.

-while manganese fluoride, MnF_2, reacts with UF_6 and WF_6, it does not with MoF_6 even at 330°C [75].

-a U. S. Patent [76] indicates that magnesium fluoride can selectively absorb MoF_6 present in trace form in UF_6, together with other volatile fluorides. Another paper [77] indicates that said absorption is low at 250°F.

-MoF_6 in solution in ClF_3 also forms complexes with cesium and ammonium fluorides. $Cs(MoF_7)$ and $NH_4(MoF_7)$ [88] are obtained. UF_6 and WF_6 yield analogous compounds.

-MoF_6, finally, forms an addition compound with sulphur tetrafluoride, SF_4 at 40°C. The solid obtained is intense yellow in color, it decomposes at a higher temperature [89]. /12

6.2. Reaction of MoF_6, WF_6 and UF_6 with the Nitrile and Nitrosyl Fluorides NO_2F, NOF and Nitrogen Oxides

These three hexafluorides react with gaseous NO_2F or NOF [82, 83, 85] to yield solid addition compounds of the form

$NO_xF \cdot MF_6$ where M can be Mo, W, U
x can be equal to 1 or 2.

Infrared data indicates that said compounds are all in ion form.

$$NO_x^+ \text{ and } MF_7^-$$

-The gaseous nitric oxide, NO, reacts with MoF_6 and UF_6 to yield the solid ion compounds [83, 84, 87].

$$NO^+(MoF_6)^- \text{ and } NO^+(UF_6)^-.$$

The same compounds are obtained by causing nitrosyl fluoride to react with MoF_5 and UF_5. On the other hand, no reaction is observed between WF_6 and NO.

-Gaseous nitrogen dioxide, NO_2 reacts with UF_6 [82, 85] to yield the solid compound NO_2UF_6, but no reaction occurs under the same conditions with MoF_6 and WF_6.

Gaseous liquid peroxide N_2O_4 reacts finally with MoF_6 and WF_6 to give, respectively, nitrosyl pentafluoromolybdate and pentafluorotungstate, white solid compounds [86].

$$2\,MoF_6 + 3\,N_2O_4 \xrightarrow{N_2O_4 \text{ liquid}} 2NOMoOF_5 + NO_2F + NOF + N_2O_5$$

$$2\,WF_6 + 3\,N_2O_4 \xrightarrow{N_2O_4 \text{ liquid}} N_3O_5W_2F_{11} + NO_2F + N_2O_5$$

The second compound decomposes at between 100-200° to yield:

$$N_3O_5W_2F_{11} \xrightarrow{100 - 200^\circ} 2\,NOWOF_5 + NOF$$

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UF_6 reacts with liquid N_2O_4 yielding solid $NOUF_6$

$$UF_{6\,(s)} + 3/2\,N_2O_{4\,(l)} \longrightarrow NOUF_{6\,(s)} + N_2O_{5\,(s)}$$

Gaseous N_2O_4 excess reacts with MoF_6 and WF_6 to yield nitrile fluoride and the nitrosyl salt [86].

$$MoF_{6\,(g)} + N_2O_{4\,(g)} \longrightarrow NOMoOF_{5\,(s)} + NO_2F_{\,(g)}$$

$$WF_{6\,(g)} + N_2O_{4\,(g)} \longrightarrow NOWOF_{5\,(s)} + NO_2F_{\,(g)}$$

UF_6 likewise reacts under the same conditions to yield $NOUF_6$.

-Nitrous oxide N_2O yields no reaction with MoF_6, WF_6 and UF_6 [84, 87].

6.3. Reaction with Nitrosyl Chloride, NOCl

NOCl reacts with MoF_6 and UF_6 to yield the nitrosyl salt $NOMoF_6$ or $NOUF_6$, on the other hand no reaction is observed with WF_6 [82, 83].

$$NOCl_{\,(g)} + MF_{6\,(g)} \longrightarrow NOMF_{6\,(g)} + \frac{1}{2}\,Cl_{2\,(g)}$$

M being Mo or U.

6.4. Oxidation-Reduction Reaction

Molybdenum hexafluoride behaves like a fluorinating agent with numerous halides. The following reactions are obtained [92, 93]

$$PF_3 \text{ and } MoF_6 \longrightarrow MoF_5 \text{ and } PF_5$$

$$CS_2 \text{ and } MoF_6 \longrightarrow MoF_5,\ (CF_3)_2\,S_2 \text{ and, } S$$

$$WF_4 \text{ and } MoF_6 \longrightarrow MoF_5 \text{ and } WF_6$$

It may thus be stated that molybdenum hexafluoride is an oxidizing agent with respect to tungsten fluoride. It is known, moreover, that UF_6 is in itself an oxidizing agent with respect to molybdenum sub-fluorides, as we have the reaction:

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$$UF_6 \text{ et } MoF_5 \longrightarrow MoF_6 \text{ and } UF_4 \quad (93) \quad (\text{or } UF_5 \text{ in excess of } UF_6)$$

The following classification is thus obtained:

1°- UF_6

2°- MoF_6

3°- WF_6

UF_6 being the greatest oxidizing agent of the three hexafluorides.

6.5. Exchange Reaction with Halides

Molybdenum hexafluoride reacts with the following compounds to yield either molybdenum pentafluoride or a molybdenum halogen fluoride [92].

PCl_3	yields	$Mo_2Cl_3F_6$, MoF_5 and PF_5 (or $MoCl_5$, PF_3 and PCl_5 in excess of MoF_6)
$AsCl_3$	yields	$Mo_2Cl_3F_6$, and AsF_3
$SbCl_3$	yields	$Mo_2Cl_3F_6$, and $SbCl_2F_3$
$TiCl_4$	yields	$Mo_2Cl_3F_6$ and TiF_4 (or $MoCl_5$, TiF_4 and Cl_2 in excess of MoF_6)
$C Cl_4$	yields	$Mo_2Cl_3F_6$, CCl_3F, CCl_2F_2 and $CClF_3$
$SiCl_4$	yields	$Mo_2Cl_3F_6$ and SiF_4
BCl_3	yields	$Mo_2Cl_3F_6$, BF_3, $BClF_2$ and BCl_2F (or $MoCl_5$, BF_3, $BClF_2$ and BCl_2F in excess of MoF_6)
PBr_2	yields	$MoBr_3$, PF_3, PF_5 and Br_2.

On the other hand MoF_6 yields no reaction with the following compounds [92, 95]

$$AsF_5,\ SoF_3,\ BiF_3.$$

6.6. Hydrolysis Reaction

Pure water hydrolyzes molybdenum hexafluoride into molybdic and hydrofluoric acids without reduction (Ruff and Ascher) [2]. Nikolaev and collaborators studied this hydrolysis reaction [97, 98]

$$MoF_6 + 2\,H_2O \qquad MoO_2F_2 + 4\,HF$$

and determined the equilibrium constant at -5°C.

$$K = 3.10^3$$

They get, under the same conditions, 6×10^2 for WF_6 and 9×10^3 for UF_6. /15

Nikolaev and collaborators likewise studied the MoF_6 - HF - H_2O system [100]; the following phases were brought out:

$H_2 MoO_2F_2 \cdot 1.5 H_2O$

$H_2 MoO_3F_2 \cdot H_2O$

$H_2 MoO_4$

In the MoF_6 hydrofluorhydric acid system the following phases appear [101]:

$H_2 MoO_3F_2 \cdot H_2O$

and $H_2 MoO_2F_4$

6.7. Relative Acidity of Molybdenum Hexafluoride

The relative acidity of an entire series of fluorides, wherein MoF_6 and WF_6 has been detected by their solubility in HF and by the ability of their solution to dissolve the fluorides classified in order of basicity [102].

6.8. Reduction of Molybdenum Hexafluoride

Ogle and Smith [103] studied the reduction of MoF_6 at 25° by the following gaseous compounds:

HCl
HBr
HI
CO

The only solid product obtained is molybdenum pentafluoride MoF_5.

The reduction of MoF_6 by hydrogen is used in the fabrication of metal objects [104] and powders [115]. Deposition is effected in several stages at temperatures ranging between 400 - 800°. A similar technique is used to manufacture binary MO - W alloys by reduction of a mixture of molybdenum and tungsten hexafluorides [105]. Metallic molybdenum can likewise be recovered from MoF_6 reduced on a heated metal plate [106], or even by electro-deposition [107]. Corrosion of nickel and its alloys by MoF_6 in a mixture with F_2 has been the object of a special study [99, 108].

MoF_6 may also be reduced by carbon [109]. CF_4 is obtained above 1,000°, /16 as well as small amounts of heavier fluorocarbons. C_2F_4 is obtained at the electric arc temperature.

With CF_2, MoF_6 is also reduced and yields CF_4 [110].

6.9. Different Uses of Molybdenum Hexafluoride

MoF_6 is used as a molybdenum halide in the manufacture of additives for lubricating mineral oils [111, 112].

MoF_6 is also used to accelerate, on the surface, the fluoridizing of aluminum objects by fluorine [113].

Finally, MoF_6 is used in the preparation of an additive to prevent parasite coloring of electrotypes used in lithography [114].

VII. Conclusions

Molybdenum hexafluoride is a volatile flouride with a symmetrical octahedral structure like many of the XY_6 formula molecules.

It crystallizes at room temperature in a body-centered cubic form. It exhibits, moreover, a low-temperature transition point below which it crystallizes in the orthorhombic system.

Melting at 17.5 and boiling at 25°C at atmospheric pressure its vapors hydrolize in contact with moist air. Like other hexafluorides, it gives additional compounds with sodium, potassium, rubidium and cesium fluorides as well as with mitrile or nitrosyl fluorides, and with nitrogen oxides. It also gives place to different oxidation-reduction reactions with numerous halides.

The sensitivity of this symmetrical molecule to hydrolysis and to reduction thus reveals its non-saturated nature, from the point-of-view of the coordination of metallic molybdenum whose greatest coordinance is 8, which contrasts with the high inertia value of similar sulphur or selenium hexafluoride molecules.

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